

Environmental impact of atmospheric NH₃ emissions under present and future conditions in the eastern United States

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[1] Recent regulations require large-scale emission reductions of NO_x and SO₂ in the eastern United States. These emission changes will alter the partitioning of ammonia between the gas and particle phases. Furthermore, ammonia emissions are expected to increase in the future. How will these changes impact the contribution of ammonia to inorganic particulate matter and nitrogen deposition? We use a chemical transport model and emission scenarios representing years 2001, 2010, and 2020 to estimate the future change of the sensitivity of iPM_{2.5} to ammonia emission reductions and change in nitrogen deposition to ecosystems. We find that during winter conditions, particulate matter concentrations in several locations in the Midwestern US continue to have significant sensitivity to NH₃ emissions. In addition, the total nitrogen deposition near NH₃ emission sources increases 10–40%. **Citation:** Pinder, R. W., A. B. Gilliland, and R. L. Dennis (2008), Environmental impact of atmospheric NH₃ emissions under present and future conditions in the eastern United States, *Geophys. Res. Lett.*, 35, L12808, doi:10.1029/2008GL033732.

1. Introduction

[2] Anthropogenic ammonia emissions significantly contribute to several well-known environmental problems. When deposited to ecosystems in excess, nitrogen, including ammonia can cause nutrient imbalances and eutrophication. In terrestrial ecosystems, this leads to a loss of plant species and habitat diversity [Smith *et al.*, 1999; Carfrae *et al.*, 2004], and in aquatic ecosystems, this leads to algal booms and hypoxia [Richardson, 1997; Paerl *et al.*, 2002]. In the atmosphere, a significant fraction of fine particulate matter is composed of ammonium nitrate and ammonium sulfate. Locations with elevated concentrations of fine particulate matter have been associated statistically with increased pulmonary and cardiac disorders [Pope, 2000].

[3] The mass of ammonium sulfate and ammonium nitrate found in particles with diameter less than 2.5 microns is known as inorganic PM_{2.5} or iPM_{2.5}. Sulfate (SO₄²⁻) is the primary oxidation product of sulfur dioxide (SO₂) emissions, and nitric acid (HNO₃) results from the oxidation of nitrogen oxide (NO) and nitrogen dioxide (NO₂) emissions (NO_x ≡ NO + NO₂). The largest sources of ammonia emissions are livestock farming operations and fertilized crops (R. Strader *et al.*, The CMU ammonia emission

inventory, 2003, available at <http://www.cmu.edu/ammonia>). In the presence of sulfate or nitric acid, ammonia will form particle ammonium sulfate and ammonium nitrate. The thermodynamics of ammonium nitrate formation is strongly dependent on temperature. In the eastern United States, nearly all of the ammonium can be found as ammonium sulfate in the summer months, and in the winter months the ammonium is often equally divided between ammonium sulfate and ammonium nitrate.

[4] While gas-phase ammonia generally has a lifetime of 1 day, fine particles generally have a lifetime between 7–10 days [Seinfeld and Pandis, 1998], which allows the ammonium to be transported far from the sources and to be deposited in comparatively pristine ecosystems. Therefore, the magnitude and spatial distribution of reduced nitrogen deposition is strongly dependent on relative partitioning between gas and particle phases.

[5] The US Environmental Protection Agency has recently promulgated a series of regulations aimed at reducing SO₂ and NO_x emissions. This includes the Clean Air Interstate Rule, Heavy-Duty Highway Diesel Program, Clean Air Nonroad Diesel Rule, and Tier 2 tailpipe standards. The current set of required emission changes have gradual deadlines, the last of which is in 2020. These programs are expected to substantially decrease sulfate and nitrate PM_{2.5} concentrations; however, some areas may require additional emission controls in order to achieve the regulatory standards of 15 μg m⁻³ annual average or 35 μg m⁻³ 24-hour average [U.S. Environmental Protection Agency (USEPA), 2005]. Previous studies have shown that ammonia emission reductions during winter can be a more effective [Tsimpidi *et al.*, 2007] and less costly [Pinder *et al.*, 2007] control strategy for PM_{2.5} than reductions in NO_x and SO₂.

[6] In this study, we examine the impact of future regulated changes in SO₂ and NO_x emissions on two important issues: (1) the sensitivity of iPM_{2.5} to ammonia emission reductions and (2) deposition of reduced nitrogen (reduced-N = NH₃ + NH₄⁺) and oxidized nitrogen (oxidized-N = NO + NO₂ + HONO + HNO₃ + NO₃⁻ + N₂O₅ + PAN + other organic nitrogen compounds). The goal is to understand how these systems will change under future scenarios of lower SO₂ and NO_x emissions and what locations may be most in need of more frequent monitoring to track and understand the trends of iPM_{2.5} concentration and nitrogen deposition.

2. Methods

[7] In this work we use the Community Multiscale Air Quality (CMAQ) chemical transport model [Byun and Schere, 2006] to simulate the fate, transport and deposition

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iPM_{2.5}, ozone, and their chemical precursors. Simulations of inorganic aerosols by CMAQ have been extensively evaluated. In a comparison with observations from 297 monitoring locations across the continental United States, Yu *et al.* [2005] conclude that CMAQ mostly captures the large-scale features of the distribution of sulfate and total nitrate concentrations. We drive the model with 2001 meteorology and three emission scenarios representing a base case and two future regulated emission reductions scenarios. The base case is 2001 emissions and the future scenarios represent 2010 and 2020. The model and the emissions are described in more detail below.

[8] CMAQ is an Eulerian model that simulates advection, dispersion, gas-phase and aqueous chemistry, aerosol thermodynamics, aerosol microphysics, heterogeneous processes, and wet and dry deposition. The inputs to the model include emissions of chemical species and meteorological conditions, and the outputs include the concentration and deposition of each species at each grid-cell for each hour. Our modeling domain includes the entire continental US with 36 by 36 km horizontal resolution and 14 vertical layers from the surface to 100 mbar. Gas-phase chemistry is simulated using the Carbon Bond IV chemical mechanism [Gery *et al.*, 1989]. We simulate one month from each season (January, April, July, October) in 2001. The meteorological inputs are derived from a 2001 simulation using the Fifth Generation Penn State/NCAR Mesoscale Model (MM5) [Grell *et al.*, 1994]. We use the same 2001 meteorology to derive the biogenic emissions and as input to CMAQ for both the year 2001 and future year scenarios.

[9] Ammonia emissions are from Gilliland *et al.* [2006]. Other emitted species are from the National Emission Inventory 1999 version 3.0 grown to 2001 levels. The 2010 and 2020 year scenarios include regulated reductions in SO₂ and NO_x emissions as described in the relevant rule documents [USEPA, 2005]. The emission changes from 2001 to the future scenarios for SO₂, NO_x, and NH₃ are shown in Figure 1.

[10] We focus especially on the impact on iPM_{2.5} in regions with high PM_{2.5} concentrations, as defined by Pinder *et al.* [2007]. These regions were selected because they represent counties that either in the past or currently did not meet US EPA's PM_{2.5} standards.

[11] To represent the uncertainty in ammonia emissions, we use an upper and lower bound centered in the base case. The bounds are set at $\pm 30\%$ to provide a reasonable range [Gilliland *et al.*, 2006] and are added to the base case and each of the future scenarios, resulting in 9 overall simulations. We then repeat every simulation with a 10% NH₃ reduction in order to estimate the sensitivity of iPM_{2.5} and nitrogen deposition to ammonia emission reductions. All of the sensitivity and uncertainty simulations are listed in Table 1.

3. Results

[12] In order to explain the future year changes in deposition and iPM_{2.5} sensitivity to ammonia emission changes, it is important to understand the changes in SO₄²⁻, NO₃⁻, and NH₄⁺. In the future emission scenarios, the July concentrations of NO₃⁻, HNO₃ and SO₄²⁻ decrease substantially (Figure 1), as would be expected with the large emission reductions. NH₄⁺ concentrations decrease, as the

effect of lower available sulfate and nitrate exceeds the effect of increased NH₃ emissions. NH₃ concentrations increase considerably, because NH₃ emissions increase and because less of the emitted NH₃ is transformed into the particle phase NH₄⁺.

[13] In the January future emission scenarios, the emission changes are similar to July, but the concentration changes differ. NO_x emission decreases cause lower HNO₃ and NO₃⁻, as in July, but the sulfate concentration increases slightly, despite large SO₂ emission reductions. We find that in the winter, the oxidation of SO₂ to sulfate is often limited by the oxidant concentrations rather than the SO₂ concentration. Since biogenic emissions are low in the winter, the production of winter ozone is often VOC limited, so decreases in NO_x lead to increases in O₃ and OH radical. This causes an increase in the gas-phase oxidation of SO₂ to form sulfate. Lower NO_x concentrations cause an increase in H₂O₂ concentrations, which increases the rate of in-cloud oxidation of SO₂. The increased rate of SO₂ to sulfate conversion offsets the SO₂ emission decrease. However, the simulated rate of sulfate production is difficult to validate using available measurements and a more comprehensive wintertime modeling and observational campaign is needed to evaluate these findings. The NH₄⁺ decrease is less than in the July case, because the January case does not have a large decrease in sulfate and total nitrate concentrations. April and October (not shown) have results similar to the average of the July and January cases.

[14] The sensitivity of iPM_{2.5} to ammonia emission reductions varies considerably over the seasons of the year under all three emission scenarios. As shown in Figure 2, January is most sensitive, July has little sensitivity, and April and October are in between. In January, much of the iPM_{2.5} is composed of ammonium nitrate. Reductions in NH₃ emissions remove both the ammonia and ammonium and cause the nitrate to return to gas-phase nitric acid. In the summer, the impact on the iPM_{2.5} mass is small. Most of the iPM_{2.5} is in the form of ammonium sulfate. Reductions in NH₃ emissions may remove available ammonia, but the sulfate can remain in the particle-phase as H₂SO₄ or HNH₄SO₄.

[15] Because the uncertainty in ammonia emissions is considerable, we have plotted the same result using the $\pm 30\%$ emission uncertainty cases as error bars. For example, the 2020 error bars are calculated as the iPM_{2.5} difference between case 15 and 16 in Table 1 for the top of the error bar, and case 17 and 18 is used for the bottom of the error bar. In Atlanta in 2020, the reduction of January iPM_{2.5} due to a 10% NH₃ emission reduction is 3% in the +30% ammonia case and 6% in the -30% ammonia case.

[16] In the future years, the sensitivity to NH₃ emissions reductions is lower compared to the present day and varies considerably for the five locations shown in Figure 2. The chemical conditions that cause this variability can be explained using the Adjusted Gas Ratio (AdjGR) [Ansari and Pandis, 1998; Pinder *et al.*, 2008]. The AdjGR is the ratio of the free ammonia to the total nitrate. The free ammonia is the sum of all ammonia that is available to form ammonium nitrate. The total nitrate is the sum of gas phase HNO₃ and particle phase NO₃⁻. When the free ammonia greatly exceeds the total nitrate concentration (AdjGR > 1), reductions in ammonia emissions cause reductions in gas-

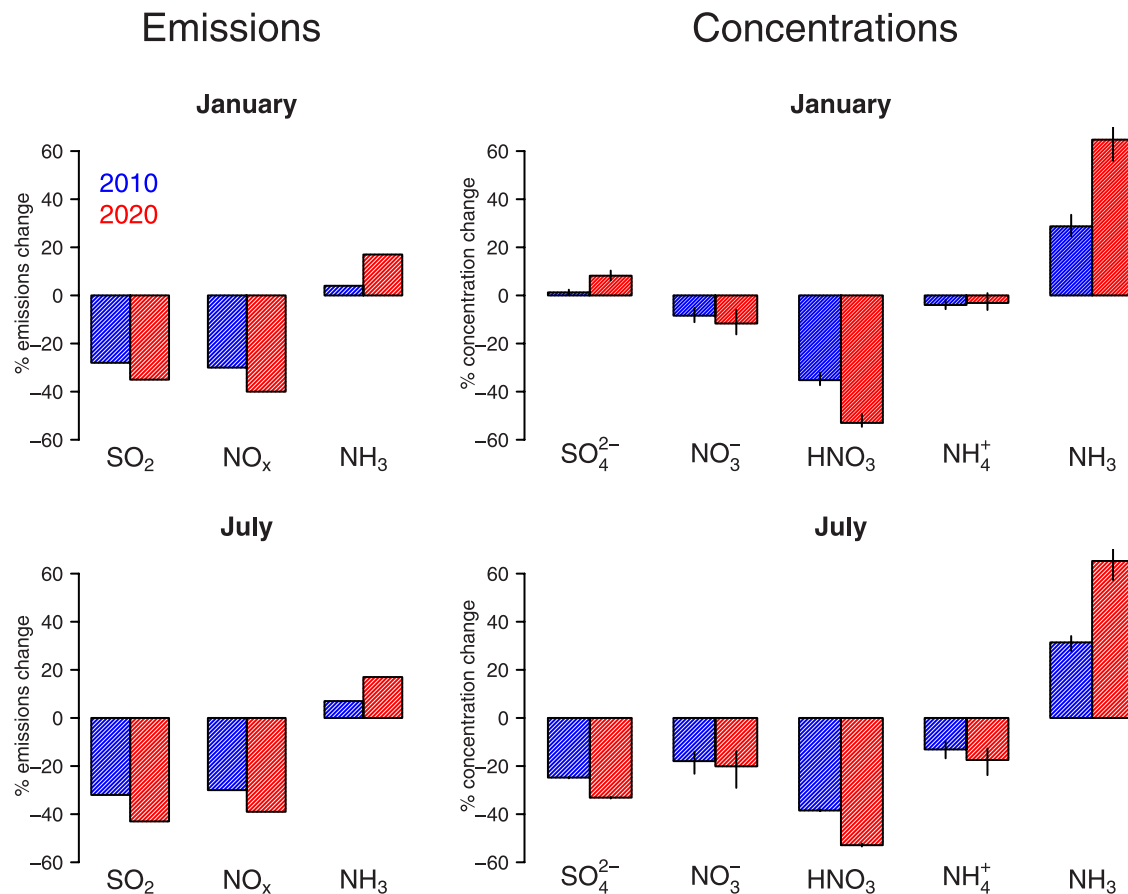


Figure 1. Change in domain wide, monthly averaged emissions and concentrations in the CMAQ simulations. The error bars in the relative concentration changes is based on the range of CMAQ results with varying NH₃ emissions by $\pm 30\%$ (see Table 1).

phase ammonia, but have little impact on $i\text{PM}_{2.5}$. Likewise, if free ammonia is scarce ($\text{AdjGR} < 1$), reductions in ammonia emissions decrease the ammonium nitrate concentration, and cause substantial reductions in $i\text{PM}_{2.5}$.

[17] The percent reduction in January $i\text{PM}_{2.5}$ due to a 10% reduction in NH₃ emissions is plotted against the AdjGR in Figure 3. Much of the variability in the $i\text{PM}_{2.5}$ sensitivity across different locations is explained by the AdjGR. For most locations, the base case (2001) AdjGR is between 1 and 2. In this transition range, the $i\text{PM}_{2.5}$ is more sensitive to total nitrate reductions, but there remains considerable sensitivity to NH₃ emission reductions.

[18] In the future scenarios, the AdjGR increases and the $i\text{PM}_{2.5}$ sensitivity decreases (Figure 3). This is expected, as reductions in NO_x emissions cause the total nitrate concentration to decrease. The future increases in NH₃ emissions coupled with only small changes in sulfate cause the free ammonia to increase. Both cause the AdjGR to become larger, which causes the $i\text{PM}_{2.5}$ to be less sensitive to an ammonia emission reduction. However, the sensitivity remains significant for many locations in the domain. For January, the reduction in $i\text{PM}_{2.5}$ for a 10% reduction in NH₃ emissions, averaged across all locations, is 5.6% in 2001 and 4.6% in 2020.

[19] The future changes in deposition are closely related to the changes in concentration and gas-particle partitioning. The increase in NH₃ emissions causes reduced-N deposition

to increase across the domain (Figure 4). The deposition increase exceeds the increase in NH₃ emissions because more of the reduced-N is in the form of gas-phase ammonium, which deposits more rapidly than particle ammonium. The deposition of oxidized-N (as moles N) decreases across the domain, as would be expected due to the NO_x emission

Table 1. NH₃ Emission Changes From 2001 Base Case for Each Sensitivity and Uncertainty Simulation^a

Number	Year	Uncertainty	Sensitivity	ΔNH_3 emissions (%)
1	2001	0	0	0
2	2001	0	-10%	-10
3	2001	+ 30%	0	+ 30
4	2001	+ 30%	-10%	+ 17
5	2001	-30%	0	-30
6	2001	-30%	-10%	-37
7	2010	0	0	+ 4
8	2010	0	-10%	-6.4
9	2010	+ 30%	0	+ 35.2
10	2010	+ 30%	-10%	+ 21.7
11	2010	-30%	0	-27.2
12	2010	-30%	-10%	-34.5
13	2020	0	0	+ 13
14	2020	0	-10%	+ 1.7
15	2020	+ 30%	0	+ 46.9
16	2020	+ 30%	-10%	+ 32.2
17	2020	-30%	0	-20.9
18	2020	-30%	-10%	-28.8

^aProjected agricultural growth cause increased NH₃ emissions in the future (see Figure 1).

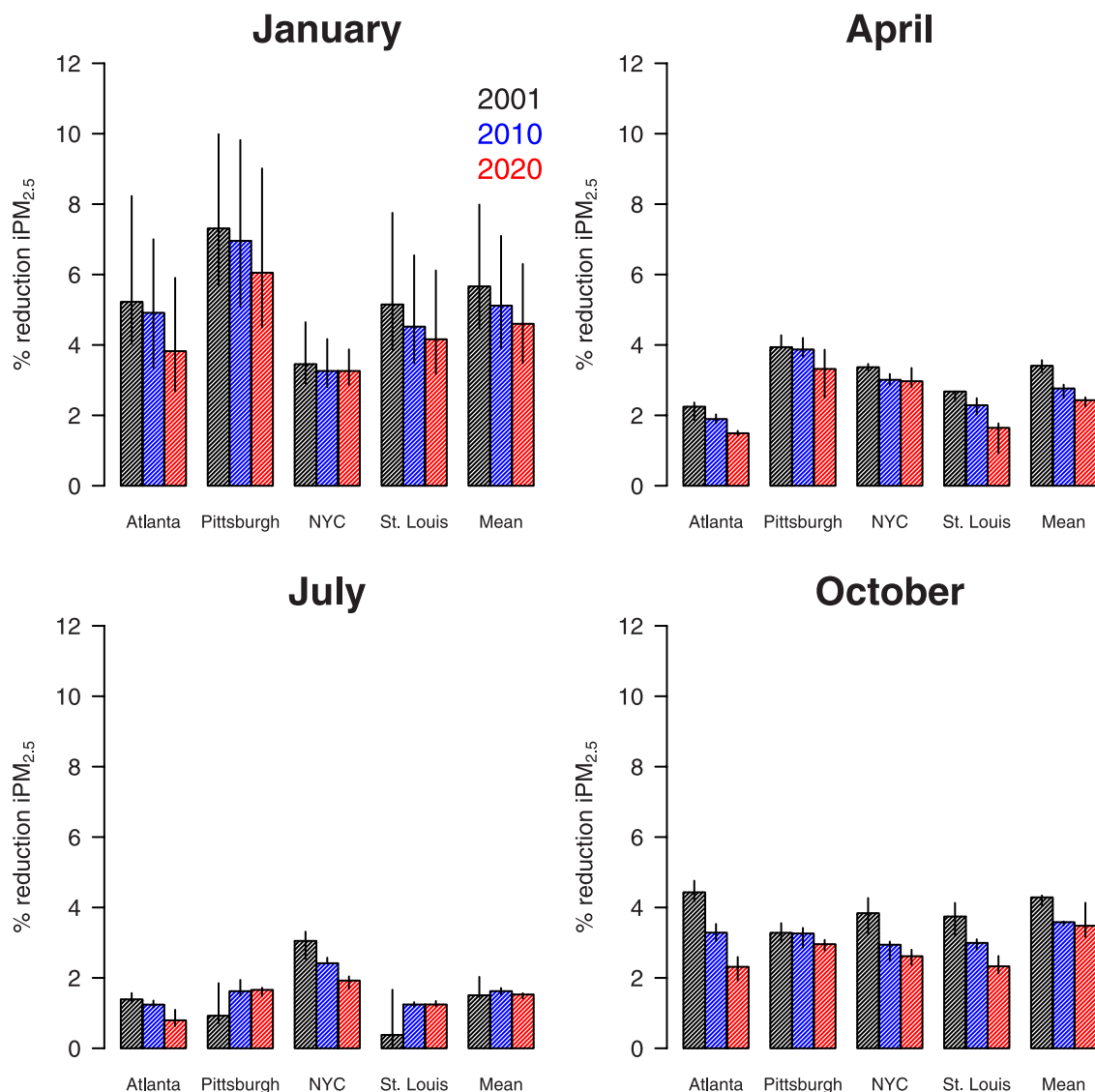


Figure 2. Reduction (%) in $iPM_{2.5}$ for a 10% reduction in NH_3 emissions at select locations and for average over high $PM_{2.5}$ areas listed in Figure 3. Error bars are the same values calculated for the low (upper bound) and high (lower bound) NH_3 emission scenarios and represent the uncertainty due to NH_3 emissions.

reductions. Because the oxidized-N deposition is larger than the reduced-N deposition, the total nitrogen (reduced + oxidized) deposition decreases in the future, except near ammonia emission sources. The largest future increases in total nitrogen deposition can be found in and around areas of high ammonia emissions, including the Delmarva Peninsula, eastern North Carolina, and northeastern Georgia. Figure 4 shows our best estimate of the spatial extent of the ammonia dry deposition changes, but the exact area of influence of these ammonia sources is dependant on uncertainties in the estimate of the ammonia dry deposition velocity.

4. Discussion

[20] Our CMAQ simulations indicate an increase in future ammonia concentration, due to an increase in emissions and because less of the emitted NH_3 is transformed to NH_4^+ . The sensitivity of $iPM_{2.5}$ to ammonia emission reductions decreases in the future, due to an increase in free ammonia and a decrease in total nitrate. However, these

sensitivities remain significant for several locations, especially in Midwestern cities upwind of the Ohio River valley. These sensitivities are greater than zero even considering $\pm 30\%$ uncertainties in NH_3 emission levels. In the future, our simulations suggest that NH_3 emission controls will continue to be an effective strategy to achieve further reductions in winter $iPM_{2.5}$, even considering the planned reductions in NO_x and SO_2 emissions.

[21] Because more of the total ammonia is in the form of gas-phase ammonia, our future simulations predict large increases in reduced-N deposition near ammonia emission sources. Many large emission sources such as livestock farming operations are heavily concentrated in sensitive watersheds, such as those feeding into the Pamlico Sound and Chesapeake Bay. In some areas, the increase in reduced-N will exceed the decrease in oxidized-N. This change will favor organisms that can most efficiently utilize N in the reduced form, which may change the frequency, intensity, toxicity, and species composition of algal blooms

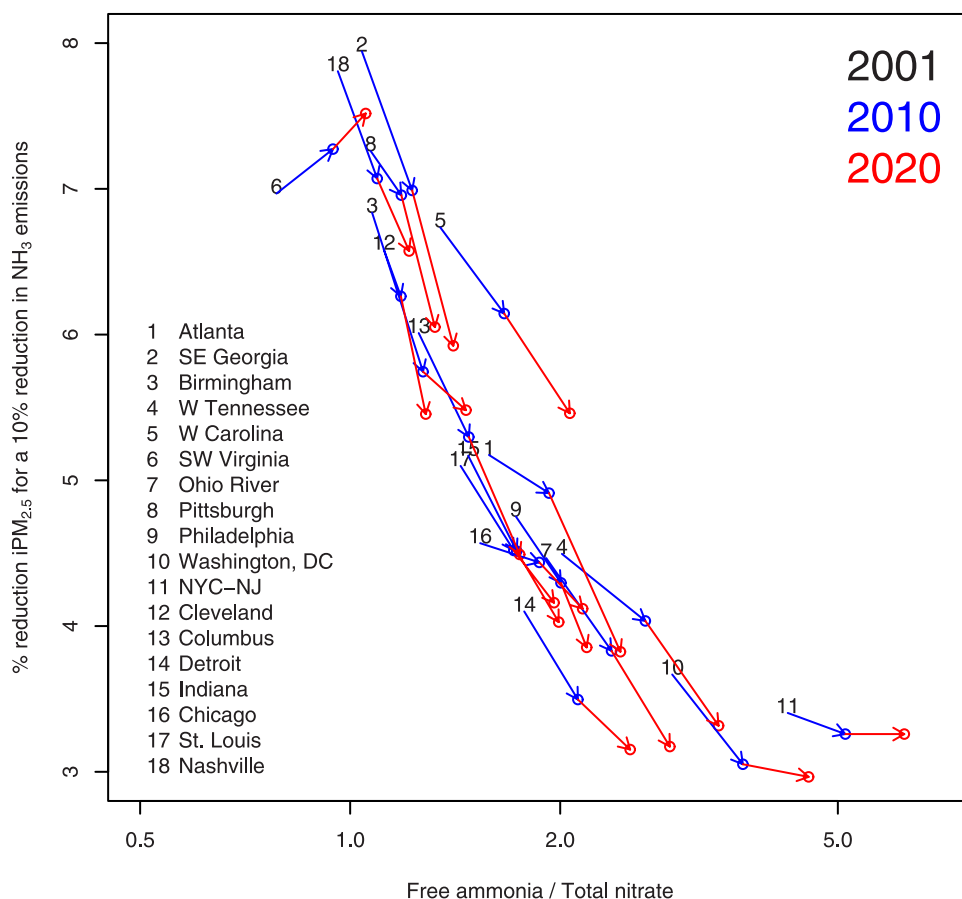


Figure 3. The January monthly-average reduction in $iPM_{2.5}$ mass for a reduction in NH_3 emissions, plotted by AdjGR. The arrows denote how the labeled location changes for 2001 (black number), 2010 (blue), and 2020 (red).

[Paerl *et al.*, 2002]. Ammonia emission controls would be an effective strategy for reducing nitrogen deposition near ammonia emission sources.

[22] While the forecasts presented here represent the state of the science, they are not a prediction of the future in an absolute sense. Instead, they represent a description of what may happen given the emission changes described in each scenario. If regulated SO_2 and NO_x emission reductions are successfully implemented and ammonia emissions continue to increase, we expect significant changes in the composi-

tion of inorganic aerosol. These changes will impact the effectiveness of $PM_{2.5}$ control strategies and the spatial pattern of nitrogen deposition. Measurements of gas phase NH_3 and HNO_3 are needed to properly monitor and track these changes and to evaluate ammonia emissions. Furthermore, our future scenarios also identify regions of increased nitrogen deposition, especially in and around regions of high ammonia emission density. Since ammonia is rarely measured routinely, additional deposition monitoring is

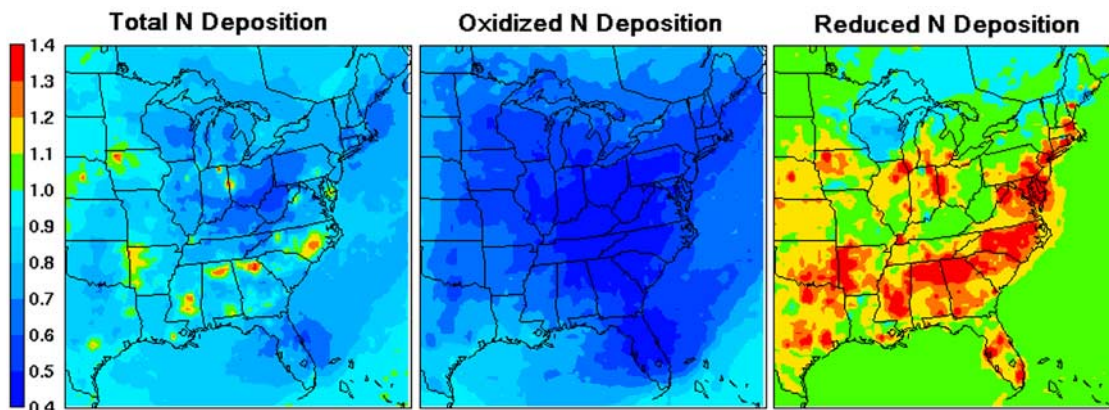


Figure 4. Ratio of 2020:2001 total, oxidized, and reduced nitrogen deposition for July.

needed in these under-sampled regions in order to assess the impacts to sensitive terrestrial and aquatic ecosystems.

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